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(54) Title of the Invention: Method for Manufacturing Polycarbonate

(57) Abstract

Constitution A method for manufacturing a polycarbonate by subjecting a divalent hydroxy compound and a bisaryl carbonate to melt polycondensation by ester interchange, characterized in that (1) a single compound produced from (a) an alkali metal compound or alkaline earth metal compound and (b) a non-volatile acid or (2) a mixture composed of (a) and (b) is used as a catalyst, and said single compound or said mixture exhibits weak acidity in an aqueous solution.

Effects Provided is a method for manufacturing a polycarbonate with improved hue and suppressed side reactions.

Claims

Claim 1 A method for manufacturing a polycarbonate by subjecting a divalent hydroxy compound and a bisaryl carbonate to melt polycondensation by ester interchange, wherein said method for manufacturing a polycarbonate is characterized in that (1) a single compound produced from (a) an alkali metal compound or alkaline earth metal compound and (b) a non-volatile acid or (2) a mixture composed of (a) and (b) is used as a catalyst, and said single compound or said mixture exhibits weak acidity in an aqueous solution.

Detailed Description of the Invention

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Field of Industrial Utilization The present invention relates to a method for manufacturing a polycarbonate by means of an ester interchange reaction. More specifically, it relates to a method for manufacturing a high molecular weight aromatic polycarbonate with improved coloring by ester interchange reaction from an aromatic diol compound and a carbonic diester.

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Prior Art and Related Problems Because of their superior impact resistance and other mechanical properties, as well as their superior heat resistance, transparency, and so on, aromatic polycarbonates have in recent years come to be widely used as engineering plastics in many different fields. One method for manufacturing these aromatic polycarbonates that has been put to industrial use is a so-called phosgene method, in which a bisphenol or other such aromatic diol is allowed to react with phosgene by interfacial polycondensation. However, phosgene methods that are currently in use in industrial settings are plagued by numerous problems, e.g., extremely toxic phosgene has to be used, a large quantity of by-product sodium chloride has to be disposed of, and health and atmospheric pollution problems are encountered with the methylene chloride that is normally used as a reaction catalyst.

0003 One known method for manufacturing an aromatic polycarbonate besides a phosgene method is a melt method, which involves an ester interchange reaction of an aromatic diol compound and a carbonic diester. This method is free of the above-mentioned problems encountered with the phosgene method, and has the advantage of allowing an aromatic polycarbonate to be manufactured less expensively. Nevertheless, with a melt method that makes use of a catalyst containing only an alkali metal compound [to produce an aromatic polycarbonate] from bisphenol A and diphenyl carbonate, for example, the phenol and diphenyl carbonate must be distilled off the high-viscosity polycarbonate melt in order to obtain a high molecular weight polycarbonate with superior mechanical properties, which means that the produced polycarbonate ends up being exposed for an extended period to a high vacuum and a high temperature, usually 250-330°C. Consequently, the alkali metal acts as a catalyst in the ester interchange reaction, and side reactions also occur, such as a decarboxylation reaction or a Kolbe-Schmitt-like reaction.

These side reactions cause branching and crosslinking, and are also a source of discoloration, so a problem generally associated with a melt method is the difficulty of obtaining a good-quality product with an excellent balance between coloring and molecular weight ("Polycarbonate Resins," published by Nikkan Kogyo Shinbunsha, Sept. 30, 1969).

0004 In an effort to solve these problems, for example, Japanese Unexamined Patent Application 4-89824 discloses a catalyst composed of (1) a nitrogen-containing basic compound, (2) an alkali metal compound or alkaline earth metal compound, and (3) boric acid or a boric ester; Japanese Unexamined Patent Application 4-46928 discloses a catalyst composed of (1) an electron donative amine compound and (2) an alkali metal compound or alkaline earth metal compound; and Japanese Unexamined Patent Application 4-175368 discloses a method in which melt polycondensation is conducted in the presence of an alkaline compound catalyst, after which an oxidative compound and an epoxy compound are added to the reaction product thus obtained. The above methods, however, do not necessarily result in a satisfactory improvement in discoloration and the like.

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Object of the Invention The present invention provides a method for manufacturing a polycarbonate by ester interchange, wherein this method for manufacturing a polycarbonate suppresses side reactions and improves the hue [of the product].

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Technological Means Used to Solve the Above-Mentioned Problems The present invention relates to a method for manufacturing a polycarbonate by subjecting a divalent hydroxy compound and a bisaryl carbonate to melt polycondensation by ester interchange, wherein said method for manufacturing a polycarbonate is characterized in that (1) a single compound produced from (a) an alkali metal compound or alkaline earth metal compound and (b) a non-volatile acid or (2) a mixture composed of (a) and (b) is used as a catalyst, and said single compound or said mixture exhibits weak acidity in an aqueous solution.

0007 Specific examples of the divalent hydroxy compound used in the present invention include 2,2-bis-(4-hydroxyphenyl)propane (hereinafter referred to as bisphenol A), bis(4-hydroxyphenyl)methane, 2,2-bis(4-hydroxyphenyl)butane, 2,2-bis(4-hydroxyphenyl)-4-methylpentane, 2,2-bis(4-hydroxyphenyl)octane, 4,4'-dihydroxy-2,2,2-triphenylethane, 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane, 2,2-bis(4-hydroxy-3-methylphenyl)propane, 2,2-bis(4-hydroxy-3-isopropylphenyl)propane, 2,2-bis(4-hydroxy-3-sec-butylphenyl)propane, 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane, 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane, 1,1'-bis-(4-hydroxyphenyl)-p-diisopropylbenzene, 1,1'-bis-(4-hydroxyphenyl)-m-diisopropylbenzene, and other bis(hydroxyaryl)cycloalkanes: 1,1-bis-(4-hydroxyphenyl)cyclohexane, 1,1-bis-(4-hydroxyphenyl)cyclopentane, and other bis-

(hydroxyaryl)cycloalkanes; and 4,4'-dihydroxydiphenyl sulfide and other bis(hydroxyaryl) sulfides. Of these, the use of bisphenol A is preferred. It is also possible to manufacture a copolymer polycarbonate by combining two or more of these divalent hydroxy compounds.

0008 Specific examples of the bisaryl compound used in the present invention include diphenyl carbonate, bis(2,4-dichlorophenyl) carbonate, bis(2,4,6-trichlorophenyl) carbonate, bis(2-cyanophenyl) carbonate, bis(o-nitrophenyl) carbonate, ditolyl carbonate, m-cresyl carbonate, dinaphthyl carbonate, and bis(diphenyl) carbonate. Of these, the use of diphenyl carbonate is preferred.

0009 Examples of the single compound produced from (a) an alkali metal compound or alkaline earth metal compound and (b) a non-volatile acid used in the present invention include potassium dihydrogenphosphate (KH_2PO_4), sodium dihydrogenphosphate (NaH_2PO_4), potassium dihydrogenphosphite (KH_2PO_3), sodium dihydrogenphosphite (NaH_2PO_3), and other salts that exhibit weak acidity.

0010 Specific examples of the (a) alkali metal compound or alkaline earth metal compound include sodium hydroxide, potassium hydroxide, lithium hydroxide, sodium carbonate, potassium carbonate, lithium carbonate, sodium acetate, potassium acetate, lithium acetate, sodium stearate, potassium stearate, lithium stearate, sodium borohydride, lithium borohydride, sodium benzoate, potassium benzoate, lithium benzoate, disodium hydrogenphosphate, dipotassium hydrogenphosphate, dilithium hydrogenphosphate, a disodium salt of bisphenol A, a dipotassium salt of bisphenol A, a dilithium salt of bisphenol A, calcium hydroxide, barium hydroxide, magnesium hydroxide, strontium hydroxide, calcium carbonate, barium carbonate, magnesium carbonate, strontium carbonate, calcium acetate, barium acetate, magnesium acetate, and strontium acetate. Of these, the use of potassium hydroxide is preferred.

0011 It is favorable for the (b) non-volatile acid to be one that will not volatilize during the preliminary reduced pressure drying or the melt polycondensation of the monomer mixture. Compounds that can be used to advantage include Lewis acid compounds, Bronsted acid compounds, and proton acids and mineral acids of these. Specific examples include hypophosphorous acid, phosphorous acid, phosphoric acid, pyrophosphoric acid, polyphosphoric acid, sulfuric acid, arsenic acid, chromic acid, molybdic acid, selenious acid, selenic acid, vanadic acid, tungstic acid, and p-toluenesulfonic acid. Of these, the use of phosphoric acid is preferred.

0012 The catalyst of the present invention is (1) a single compound produced from (a) an alkali metal compound or alkaline earth metal compound and (b) a non-volatile acid or (2) a mixture composed of (a) an alkali metal compound or alkaline earth metal compound and (b) a non-volatile acid, and the above-mentioned single compound or mixture must exhibit weak

acidity in an aqueous solution. The extent of the weak acidity should be such that the pH is between 3.0 and 6.5 at room temperature when the concentration of alkali metal compound or alkaline earth metal compound is 0.1 mol/L, for example. If the pH in this case is less than 3.0, the polymerization of the polycarbonate will be slow and the product will not have a high molecular weight. On the other hand, if the pH is over 6.5, discoloration will tend to occur, and a polycarbonate with a good hue may not be obtained. Salts that exhibit weak acidity by themselves, such as potassium dihydrogenphosphate, can be used by themselves.

0013 The catalyst of the present invention is prepared as an aqueous solution, but a hydrolysis reaction will generally proceed if water is present in an ester interchange reaction. Accordingly, it is preferable for water not to be present under the high-temperature conditions at which an ester interchange reaction will proceed between a dihydric phenol (such as bisphenol A) and a bisaryl carbonate. Therefore, it is preferable for the catalyst to be added to the monomer mixture at room temperature, and the water then to be substantially removed by reduced pressure drying, usually at a temperature of 150°C or lower, and preferably at a temperature of 100°C or lower.

0014 The alkali metal compound or alkaline earth metal compound is usually used in an amount (as the amount of alkali metal or alkaline earth metal) of 1×10^{-7} to 1×10^{-3} mol, and preferably 1×10^{-6} to 1×10^{-4} mol, per mole of dihydric phenol present in the reaction system.

0015 The amount in which the bisaryl carbonate is used is usually 1 to 1.3 mol, and preferably 1.01 to 1.2 mol, per mole of divalent hydroxy compound.

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Working Examples

Working examples of the present invention will now be described.

Measurement methods: The physical property measurements and test methods mentioned in the working examples of the present invention were as follows.

(1) Intrinsic viscosity (η_{inh}): This was measured using a Canon Fenske type of viscometer, in chloroform, at 30°C, and at a concentration of 0.5 g/dL. η_{inh} was computed from the following equation: $\eta_{inh} = \ln(t/t_0)/c$, where t_0 is the drop time of chloroform, t is the drop time of the sample solution, and c is the concentration of the sample.

(2) Glass transition temperature (T_g): Using a DSC220C apparatus made by Seiko Denshi Kogyo, the temperature of the sample was raised at 10°C/min in nitrogen, and the inflection point of the endothermic curve was termed T_g .

(3) Hue ($A_{350} - A_{600}$): Using a model 330 auto-recording spectrophotometer made by Hitachi, the difference in absorbancy ($A_{350} - A_{600}$) of a 10% methylene chloride solution of polycarbonate at wavelengths of 350 and 600 nm was measured. The greater is this value, the greater the discoloration.

0017 Working Example 1

22.8 g (0.1 mol) of bisphenol A that had been washed with methylene chloride and then purified by recrystallization with a mixed solution of toluene and ethanol, 22.7 g (0.106 mol) of diphenyl carbonate that had been washed with 80°C hot water and then purified by reduced pressure distillation, and 29 μL (2.9×10^{-6} mol as metallic potassium) of a 0.1 mol/L aqueous solution of potassium dihydrogenphosphate were put in a 100 mL reactor made of SUS316, the system was dried under reduced pressure for 30 minutes at 200°C under a nitrogen gas flow, the temperature was raised while the pressure was gradually reduced, and melt polycondensation was conducted at a final pressure of 0.1 torr and temperature of 270°C. The phenol thus produced was distilled off to yield a polycarbonate. The polycarbonate thus obtained was a tough, colorless, transparent polymer with an η_{inh} of 0.443, a Tg of 145°C, and an ($A_{350} - A_{600}$) of 0.015.

0018 Working Example 2

Other than using 59 μL (5.9×10^{-6} mol as metallic potassium) of an aqueous solution composed of potassium hydroxide and phosphoric acid, whose pH had been adjusted to 4.0 at a metallic potassium concentration of 0.1 mol/L, a reaction was conducted in the same manner as in Working Example 1. The polycarbonate thus obtained was a tough, colorless, transparent polymer with an η_{inh} of 0.378, a Tg of 142°C, and an ($A_{350} - A_{600}$) of 0.012.

0019 Working Example 3

Other than using 29 μL (2.9×10^{-6} mol as metallic potassium) of an aqueous solution composed of potassium hydroxide, whose pH had been adjusted to 5.1 at a metallic potassium

concentration of 0.1 mol/L, a reaction was conducted in the same manner as in Working Example 1. The polycarbonate thus obtained was a tough, colorless, transparent polymer with an η_{inh} of 0.532, a Tg of 150°C, and an ($A_{350} - A_{600}$) of 0.016.

0020 Working Example 4

Other than using 29 μL (2.9×10^{-6} mol as metallic potassium) of an aqueous solution composed of potassium hydroxide and sulfuric acid, whose pH had been adjusted to 4.5 at a metallic potassium concentration of 0.1 mol/L, a reaction was conducted in the same manner as in Working Example 1. The polycarbonate thus obtained was a tough, colorless, transparent polymer with an η_{inh} of 0.332, a Tg of 141°C, and an ($A_{350} - A_{600}$) of 0.016.

0021 Comparative Example 1

Other than using 29 μL (2.9×10^{-6} mol as metallic potassium) of an aqueous solution composed of potassium hydroxide and phosphoric acid, whose pH had been adjusted to 2.5 at a metallic potassium concentration of 0.1 mol/L, a reaction was conducted in the same manner as in Working Example 1. Almost no phenol production was noted, and a polycarbonate was not obtained.

0022 Comparative Example 2

Other than using 29 μL (2.9×10^{-6} mol as metallic potassium) of an aqueous solution composed of potassium hydroxide and phosphoric acid, whose pH had been adjusted to 9.0 at a metallic potassium concentration of 0.1 mol/L, a reaction was conducted in the same manner as in Working Example 1. The polycarbonate thus obtained was a tough polymer with an η_{inh} of 0.620 and a Tg of 151°C, but it was slightly discolored to yellow, and had an ($A_{350} - A_{600}$) of 0.138.